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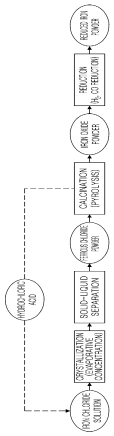
(54) METHOD FOR MANUFACTURING NEEDLE-SHAPED OR ROD-SHAPED POROUS IRON POWDER AND NEEDLE-SHAPED OR ROD-SHAPED POROUS IRON POWDER MANUFACTURED THEREBY

(57) The present invention relates to a method for manufacturing a needle-shaped or rod-shaped porous iron powder. Specifically, the present invention provides a method for manufacturing a needle-shaped or rod-shaped porous iron powder and a needle-shaped or rod-shaped porous iron powder manufactured thereby, the method comprising the steps of: preparing a ferrous dichloride chloride by concentrating a ferrous chloride aqueous solution; solid-liquid separating the ferrous dichloride to prepare ferrous dichloride powder; oxidizing the ferrous dichloride powder; and reducing the oxidized ferrous dichloride.

[FIG. 1]



EP 3 878 580 A1

Description

[Technical Field]

[0001] The present disclosure relates to a method for manufacturing a needle-shaped or rod-shaped porous iron powder and a needle-shaped or rod-shaped porous iron powder manufactured thereby. More particularly, the present disclosure relates to a method for manufacturing a needle-shaped or rod-shaped porous iron powder using a ferrous chloride aqueous solution and a needle-shaped or rod-shaped porous iron powder manufactured thereby.

[Background Art]

[0002] Conventionally, as a method for manufacturing iron powder, there is a sponge-iron process and a water-atomizing process. The sponge-iron process is a process of reducing iron oxide to produce a porous iron powder and the water-atomizing process is a process of using a high-pressure water jet to atomize molten iron, and the iron powder manufactured therefrom is not a porous powder but a dense powder. In addition, most of the powders manufactured therefrom have an angled cube shape, a spherical shape, or a non-uniform shape.

[0003] For the iron oxide used in the sponge-iron process, an iron ore, a powder produced during an iron manufacturing process, iron oxide manufactured using a post-pickling solution produced after surface pickling during an iron plate manufacturing process, or the like, may be used as a raw material, and since a porous iron powder manufactured by the sponge-iron process has a large specific surface area, high reactivity, and strong reducibility, the porous iron powder may be used in self-lubricating bearing materials; materials for purifying soil, ground water, or industrial wastewater (such as a catalyst and reducing agent); welding rod coating materials; pocket warmer materials; a deoxidizer; a raw materials for preparing iron compounds; an extractant for cementation; and the like.

[0004] Meanwhile, U.S. Patent Publication No. 2016-0096739 uses a method for manufacturing an iron powder by a ferrous chloride aqueous solution, but when a method for manufacturing a needle-shaped or rod-shaped porous iron powder from the ferrous chloride aqueous solution is developed, it is expected that the method will be used more usefully in the field of using an iron powder.

[Disclosure]

[Technical Problem]

[0005] An aspect of the present disclosure is to provide a method for manufacturing an iron powder having both a needle shape or rod shape characteristic and a porous characteristic.

[0006] Another aspect of the present disclosure is to provide an iron powder manufactured by the manufacturing method of the present disclosure.

[Technical Solution]

[0007] According to an aspect of the present disclosure, a method for manufacturing a needle-shaped or rod-shaped porous iron powder includes: concentrating a ferrous chloride aqueous solution to prepare a ferrous chloride dihydrate; subjecting the ferrous chloride dihydrate to a solid-liquid separation to prepare a ferrous chloride dihydrate powder; oxidizing the ferrous chloride dihydrate powder; and reducing the oxidized ferrous chloride dihydrate.

[0008] According to another aspect of the present disclosure, a needle-shaped or rod-shaped porous iron powder manufactured by the manufacturing method is provided.

[Advantageous Effects]

[0009] According to the process of the present disclosure, an iron powder may be mass-produced from an iron chloride aqueous solution, and the thus-manufactured iron powder has a porous needle shape or rod shape and may be used in the conventional porous iron powder application fields, of course, and also may obtain filling rate improvement, workability improvement, physical property improvement, and the like based on the characteristics of the rod-shaped powder.

[Description of Drawings]

[0010]

FIG. 1 is a schematic flow chart of a method for manufacturing a needle-shaped or rod-shaped porous iron powder of the present disclosure.

FIG. 2 is an image of ferrous chloride dihydrate and ferrous chloride tetrahydrate crystals shown in the concentration of a ferrous chloride aqueous solution according to an exemplary embodiment of the present disclosure, taken by SEM.

FIG. 3 is an image of an iron oxide powder obtained after subjecting ferrous chloride dihydrate obtained by the concentration of the ferrous chloride aqueous solution according to an exemplary embodiment of the present disclosure to a calcination process, taken by SEM.

FIG. 4 is an image of a reduced iron powder obtained after subjecting an iron oxide powder according to an exemplary embodiment of the present disclosure to a reduction reaction, taken by SEM.

[Best Mode for Invention]

[0011] Hereinafter, preferred embodiments of the present disclosure will now be described in detail with reference to the accompanying drawings. However, the embodiments of the present disclosure may be modified in many different forms and the scope of the present disclosure should not be limited to the embodiments set forth herein.

[0012] The present disclosure provides a method for manufacturing an iron powder having both a needle shape or rod shape characteristic and a porous characteristic and iron powder manufactured by the manufacturing method.

[0013] Specifically, the method for manufacturing a needle-shaped or rod-shaped porous iron powder of the present disclosure provides a method for manufacturing a needle-shaped or rod-shaped porous iron powder including: concentrating a ferrous chloride aqueous solution to prepare a ferrous chloride dihydrate; subjecting the ferrous chloride dihydrate to a solid-liquid separation to prepare a ferrous chloride dihydrate powder; oxidizing the ferrous chloride dihydrate powder; and reducing the oxidized ferrous chloride dihydrate.

[0014] A raw material of the ferrous chloride aqueous solution may be a post-solution produced after a pickling process for removing oxides on a surface during an iron plate manufacturing process, a post-solution produced during other processes, or an aqueous solution in which iron is dissolved in hydrochloric acid, and it is preferred that the ferrous chloride aqueous solution may not be a saturated or supersaturated aqueous solution.

[0015] A concentration of the ferrous chloride aqueous solution is 20 to 625 g/L, preferably 250 to 600 g/L. When the concentration is less than 20 g/L, an amount of ferrous chloride in the aqueous solution is low, energy to evaporate moisture during concentration is excessively consumed and an amount of precipitated ferrous chloride dihydrate is small, and when the concentration is more than 625 g/L, the ferrous chloride aqueous solution is saturated or supersaturated to cause precipitation during transport.

[0016] The step of preparing ferrous chloride dihydrate is to concentrate the ferrous chloride aqueous solution to precipitate supersaturated ferrous chloride dihydrate, and the concentration at this time may be carried out by evaporative concentration.

[0017] Meanwhile, in the solid-liquid separation carried out in the step of preparing a ferrous chloride dihydrate powder, the precipitated ferrous chloride dihydrate may be separated, for example, using a centrifuge, but the present disclosure is not limited thereto, and the solid-liquid separation may be carried out by any method which may be used for the solid-liquid separation in the art, such as filtration.

[0018] When the step of preparing ferrous chloride dihydrate is carried out by evaporative concentration, a temperature in a concentration process should be adjusted, and it is preferred that the evaporative concentration herein is carried out at a temperature of, for example, 72 to 125°C, preferably 75 to 95°C. When the evaporative concentration is carried out at a temperature of lower than 72°C, ferrous chloride tetrahydrate may be precipitated and the ferrous chloride tetrahydrate is precipitated in the form of an angled polyhedron, and at a temperature of higher than 125°C, iron chloride monohydrate is produced and energy is excessively consumed. An image of the ferrous chloride tetrahydrate precipitated in the form of an angled polyhedron, taken by SEM is shown in FIG. 2.

[0019] The step of oxidizing a ferrous chloride dihydrate powder may be carried out by a calcination process in which a pyrolysis reaction is carried out under an oxygen atmosphere. In the calcination process, a reaction of ferrous chloride dihydrate with oxygen is as follows:

$$2\,(FeCl_2H_2O) + 1/2O_2 \rightarrow Fe_2O_3 + 4HCl\,(g)$$

[0020] Here, an oxide of Fe_3O_4 or FeO may be rarely produced as well as Fe_2O_3 by the reaction above.

[0021] In addition, although the calcination process is not limited, a reaction furnace such as a fluidized furnace, a rotary kiln, a belt furnace, and a drop tube furnace may be used, and it is necessary to minimize crushing of powder by an action of external force on the powder during the reaction to maintain the form of a rod shape.

[0022] Furthermore, the reaction of the calcination process may be carried out at a temperature of 200 to 1300°C. At a temperature of lower than 200°C, iron oxide is not produced, and at a temperature higher than 1300°C, iron oxide

sintering occurs so that it is difficult to obtain iron oxide having a desired shape. The reaction may preferably be carried out at a temperature of 500 to 800°C.

[0023] Classification may be carried out for dividing the shape of iron oxide produced by the calcination process. Furthermore, hydrochloric acid produced in the process may be wet-collected to prepare a hydrochloric acid aqueous solution, which may be used in preparation of the ferrous chloride aqueous solution.

[0024] The step of reducing the oxidized ferrous chloride dihydrate may be carried out by subjecting the oxidized ferrous chloride dihydrate to a reduction reaction under a high temperature reducing atmosphere. Here, the reducing atmosphere may be, for example, an atmosphere of hydrogen, carbon monoxide, or a mixed gas thereof, and a compound which may produce hydrogen, carbon monoxide, or a mixed gas thereof by a reaction such as decomposition may be used as a reducing agent. The reduction reaction is, for example, as follows:

$$Fe_2O_3 + 3H_2\ (g) \text{ or } 3CO(g) \rightarrow 2Fe + 3H_2O\ (g) \text{ or } 3CO_2\ (g)$$

[0025] Here, an oxide of Fe_3O_4 or FeO which is rarely produced in the oxidation step undergoes a reduction reaction by the following reaction:

$$FeO + H_2\ (g) \text{ or } CO\ (g) \rightarrow Fe + H_2O\ (g) \text{ or } CO_2\ (g)$$

$$Fe_3O_4 + 4H_2\ (g) \text{ or } 4CO\ (g) \rightarrow 3Fe + 4H_2O\ (g) \text{ or } 4CO_2\ (g)$$

[0026] In addition, though the reduction process is not limited, a reaction furnace such as a fluidized furnace, a rotary kiln, a belt furnace, and a drop tube furnace may be used, and it is necessary to minimize crushing of powder by an action of external force on the powder during the reaction to maintain the form of a rod shape.

[0027] Furthermore, the reduction reaction may be carried out at a temperature of 400 to 1300°C. It is because at a temperature less than 400°C, a reaction rate is low so that productivity is decreased, and at a temperature higher than 1300°C, sintering of reduced iron produced may excessively occur or a reduced iron microstructure is coarsened so that a porous structure disappears. When the reducing atmosphere is a hydrogen atmosphere, the reduction reaction may preferably be carried out at a temperature of 600 to 800°C, and when the reducing atmosphere is a carbon monoxide atmosphere, the reduction reaction may preferably be carried out at a temperature of 700 to 1000°C.

[0028] Classification may be carried out for dividing the shape of iron oxide produced by the reduction reaction. Furthermore, since the prepared reduced iron may have good reactivity to cause reoxidation, a powder should be collected under an inert atmosphere.

[0029] The needle-shaped or rod-shaped porous iron powder manufactured by the manufacturing method of the present disclosure has a specific surface area of 0.3 to 3 m^2/g, preferably 0.5 to 2.5 m^2/g. When the specific surface area of the iron powder is less than 0.3 m^2/g, reactivity is low, and when the specific surface area is more than 3 m^2/g, oxidation or ignition easily occurs in the atmospheric state so that handling is difficult in the process.

[0030] Hereinafter, the present disclosure will be described in detail through the specific examples. The following example is only illustrative for assisting in the understanding of the present disclosure, and the scope of the present disclosure is not limited thereto.

[Mode for Invention]

Examples

[0031] A ferrous chloride ($FeCl_2$) aqueous solution produced in a nickel hydrometallurgical process was used to manufacture a needle-shaped or rod-shaped iron powder. An exemplary process is shown in FIG. 1, and a specific process is as follows.

[0032] A ferrous chloride aqueous solution (concentration: 220 g/L) was concentrated to precipitate ferrous chloride dihydrate ($FeCl_2.2H_2O$). The precipitated ferrous chloride dihydrate was subjected to a solid-liquid separation by a centrifugation method to separate a ferrous chloride dihydrate powder. Here, aqueous solution concentration was carried out at a temperature of 80°C.

[0033] An image of a ferrous chloride dihydrate crystal prepared in this step, taken by SEM is shown in FIG. 2.

[0034] Next, the ferrous chloride dihydrate powder was added to a rotary kiln and calcined by a pyrolysis reaction under a high temperature atmosphere including oxygen. Thus, needle-shaped or rod-shaped iron oxide was manufactured therefrom.

[0035] The calcination process was carried out at 700°C for 90 minutes, and classification was carried out for dividing a shape of the needle-shaped or rod-shaped iron oxide produced. In addition, an oxide of Fe_3O_4 or FeO may also be rarely produced as well as Fe_2O_3. Meanwhile, HCl produced together in the rotary kiln was collected by a scrubber and

reused in a nickel smelting process.

[0036] An image of oxidized iron powder produced by the above process, taken by SEM is shown in FIG. 3.

[0037] Next, the needle-shaped or rod-shaped iron oxide was injected with a mesh belt and a reduced iron powder was manufactured by a reduction reaction in a high temperature gas reducing atmosphere. Here, the gas reducing atmosphere was a hydrogen or carbon monoxide atmosphere.

[0038] The reduction reaction was carried out at 750°C for 60 minutes and classification was carried out for dividing the shape of needle-shaped or rod-shaped iron oxide produced to divide the powder into a needle-shaped or rod-shaped reduced iron powder and a fine reduced iron powder.

[0039] The produced needle-shaped or rod-shaped reduced powder was a powder having a length of about 500 μm and an aspect ratio of about 5 and had a specific surface area of about 2.3 m^2/g. Here, since the prepared reduced iron may have good reactivity to cause reoxidation, the powder should be collected under an inert atmosphere.

[0040] An image of reduced iron powder produced by the above process, taken by SEM is shown in FIG. 4.

[0041] Hereinabove, the exemplary embodiments of the present disclosure were described in detail, however, the scope of a right of the present disclosure is not limited thereto, and it is apparent to a person skilled in the art that various modifications and changes are possible within the scope not departing from the technical idea of the present disclosure.

Claims

1. A method for manufacturing a needle-shaped or rod-shaped porous iron powder, the method comprising:

   concentrating a ferrous chloride aqueous solution to prepare a ferrous chloride dihydrate;
   subjecting the ferrous chloride dihydrate to a solid-liquid separation to prepare a ferrous chloride dihydrate powder;
   oxidizing the ferrous chloride dihydrate powder; and
   reducing the oxidized ferrous chloride dihydrate.

2. The method for manufacturing a needle-shaped or rod-shaped porous iron powder of claim 1, wherein the ferrous chloride aqueous solution has a concentration of 20 to 625 g/L.

3. The method for manufacturing a needle-shaped or rod-shaped porous iron powder of claim 1, wherein the concentrating of the ferrous chloride aqueous solution is carried out by evaporative concentration at a temperature of 72 to 125°C.

4. The method for manufacturing a needle-shaped or rod-shaped porous iron powder of claim 1, wherein the oxidizing of the ferrous chloride dihydrate powder is carried out by calcination at a temperature of 200 to 1300°C in an oxygen atmosphere.

5. The method for manufacturing a needle-shaped or rod-shaped porous iron powder of claim 1, wherein the reducing of the ferrous chloride dihydrate powder is carried out at a temperature of 400 to 1300°C under a reducing atmosphere.

6. The method for manufacturing a needle-shaped or rod-shaped porous iron powder of claim 5, wherein the reducing atmosphere is an atmosphere of hydrogen, carbon monoxide, or a mixed gas thereof.

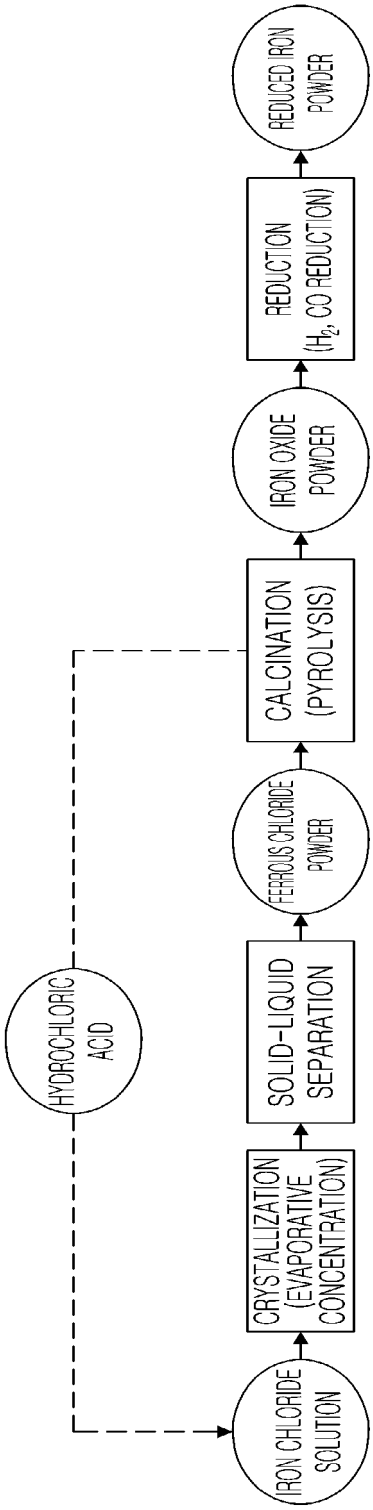
7. The method for manufacturing a needle-shaped or rod-shaped porous iron powder of claim 6, wherein the reducing of the ferrous chloride dihydrate powder is carried out at a temperature of 600 to 800°C in the case of the hydrogen atmosphere.

8. The method for manufacturing a needle-shaped or rod-shaped porous iron powder of claim 6, wherein the reducing of the ferrous chloride dihydrate powder is carried out at a temperature of 700 to 1000°C in the case of the carbon monoxide atmosphere.

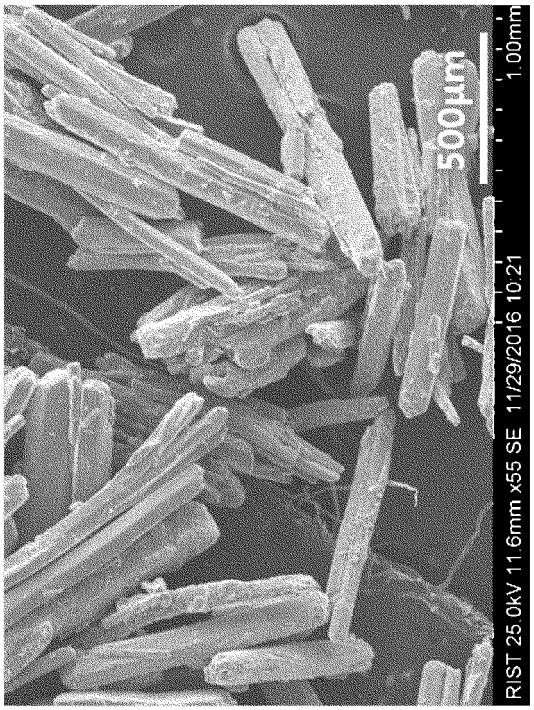
9. A needle-shaped or rod-shaped porous iron powder manufactured by the method of any one of claims 1 to 8.

10. The needle-shaped or rod-shaped porous iron powder of claim 9, wherein the iron powder has a specific surface of 0.3 to 3 m^2/g.

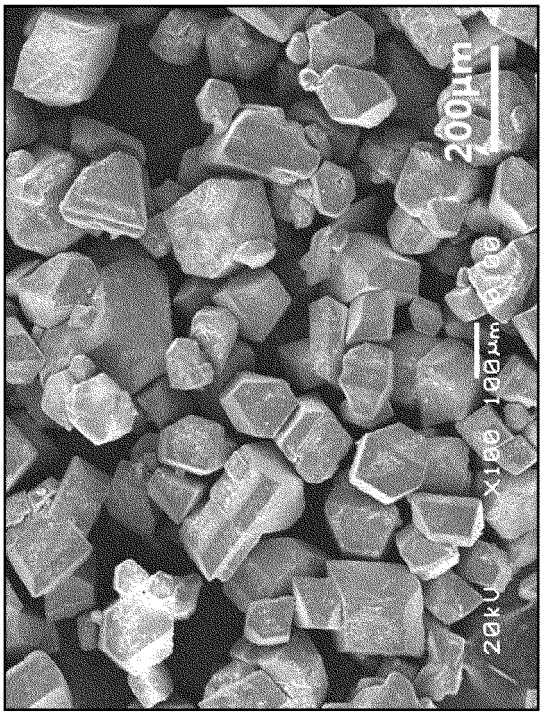
[FIG. 1]


REDUCED IRON POWDER
REDUCTION (H_2, CO REDUCTION)
IRON OXIDE POWDER
CALCINATION (PYROLYSIS)
FERROUS CHLORIDE POWDER
SOLID-LIQUID SEPARATION
CRYSTALLIZATION (EVAPORATIVE CONCENTRATION)
IRON CHLORIDE SOLUTION
HYDROCHLORIC ACID

[FIG. 2]

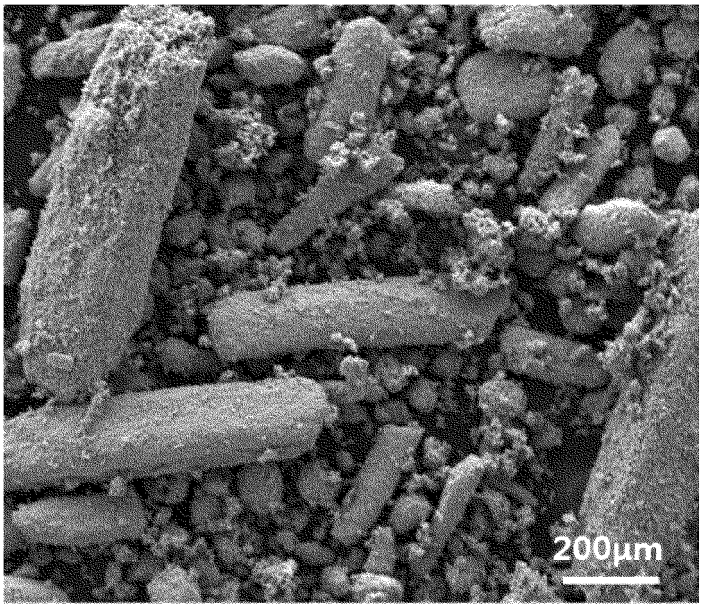


$[FeCl_2 \cdot 2H_2O$ CRYSTAL SHAPE]



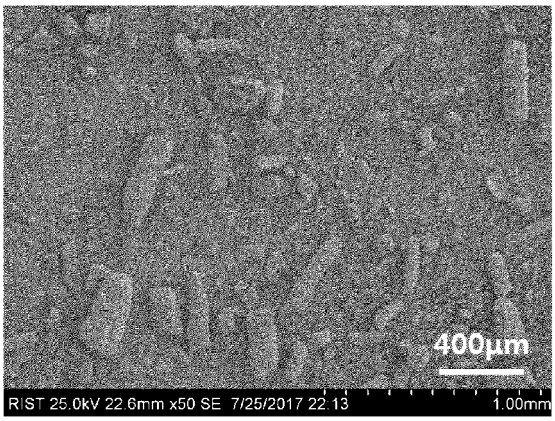
$[FeCl_2 \cdot 4H_2O$ CRYSTAL SHAPE]

[FIG. 3]

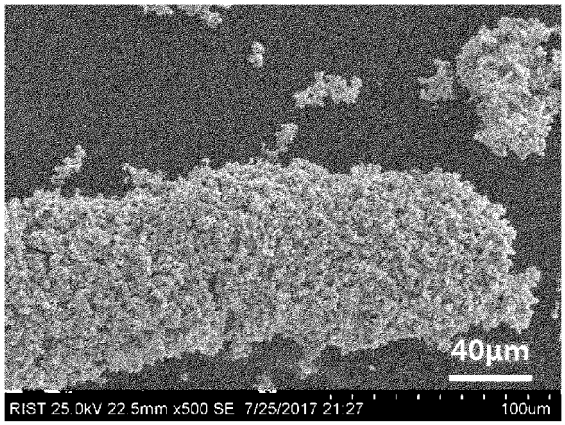


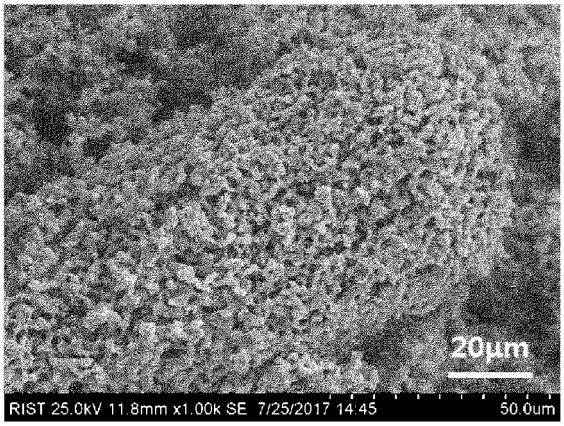
[Fe_2O_3 CRYSTAL SHAPE AFTER CALCINATION]

[FIG. 4]



[Fe POWDER SHAPE AFTER REDUCTION]





[Fe POWDER MICROSTRUCTURE AFTER REDUCTION]

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2019/014795

A. CLASSIFICATION OF SUBJECT MATTER

B22F 9/24(2006.01)i, B22F 1/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F 9/24; B22F 1/00; B22F 9/22; C01G 49/02; C01G 49/06; C21B 13/00; C22C 33/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & Keywords: iron powder, manufacturing, ferrous chloride, concentration and solid liquid separation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-1798731 B1 (POSCO et al.) 17 November 2017 See paragraphs [0025]-[0058].	1-10
Y	KR 10-2018-0082760 A (AGENCY FOR DEFENSE DEVELOPMENT) 19 July 2018 See claims 1, 2, 4; table 1 and figure 5.	1-10
Y	KR 10-1995-0006268 B1 (KIM, Mi-la et al.) 13 June 1995 See page 2, lines 25-32; page 3, lines 1-3.	8
A	JP 2005-145757 A (NISSHIN STEEL CO., LTD.) 09 June 2005 See claim 1.	1-10
DA	US 2016-0096739 A1 (INNOVA POWDERS INC.) 07 April 2016 See claim 1.	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 FEBRUARY 2020 (07.02.2020)	**10 FEBRUARY 2020 (10.02.2020)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex Daejeon Building 4, 189, Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2019/014795

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-1798731 B1	17/11/2017	KR 10-2017-0076853 A	05/07/2017
KR 10-2018-0082760 A	19/07/2018	KR 10-1924274 B1	30/11/2018
KR 10-1995-0006268 B1	13/06/1995	KR 10-1995-0003453 A	16/02/1995
JP 2005-145757 A	09/06/2005	None	
US 2016-0096739 A1	07/04/2016	None	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20160096739 A **[0004]**